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Seasonal variability of trace metals in the Lena River and the southeastern Laptev Sea: Impact of the spring freshet

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Abstract

The distribution of dissolved and particulate trace metals (Fe, Mn, Cu, Ni, Zn, and Pb) was studied for the first time during the spring high flow period of the Lena River (Arctic Siberia). The results show that concentrations of dissolved metals in the river Lena during the spring high flow in June 1996 (spring freshet) were significantly higher than those reported for the rest of the year. For example the measured average concentration of dissolved Fe (6349 ± 2122 nM) during the high flow is approximately 7 times higher than previously published concentrations measured during the summer months. Dissolved Fe concentrations in the freshwater (salinity <1) are positively correlated with the amount of suspended particulate matter (SPM) ($p<0.01$), but negatively correlated with the Fe concentrations in SPM ($p<0.01$).

The data showed that the aluminium-normalized concentrations of particulate Fe, Mn, Pb, Ni, and Zn in the freshwater are negatively correlated with SPM. This suggests that the mobilization of metals from suspended particulate matter is the driving force for the observed high concentrations of dissolved Fe, Mn, Zn and Pb in the water of the Lena River during the spring freshet.

During the high flow period in June about 35% of the total annual flow of the river Lena flows into the Laptev Sea. Previously published metal budgets for the river Lena that did not incorporate data from the spring high flow period, therefore, underestimate the fluxes of dissolved trace metals from the Siberian rivers to the Arctic Ocean. For instance, the estimated input of dissolved Fe in June 1996 is approximately 4.5 times higher than the average annual dissolved Fe input calculated on the basis of summer data. The results of this study demonstrate that the previous evaluations of the trace metal flux of the Lena river–which are based on data obtained from August to October–may underestimate the total riverine input of dissolved trace metals to the Arctic Ocean.

Keywords: Arctic; Lena River; Laptev Sea; trace elements; seasonal variability

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1. Introduction

The Arctic receives ~10% of the freshwater and dissolved organic matter supplied globally by rivers, yet it represents only 1% of the global ocean volume (Opsahl et al., 1999). Climate change has already altered the freshwater discharge to the Arctic Ocean (Peterson et al., 2002) and may also affect the flux of inorganic nutrients, organic compounds (Dittmar and Kattner, 2003), and contaminants (Macdonald et al., 2003). With respect to these changes a better understanding of the processes controlling trace metal input and cycling in natural waters is crucial to assess and anticipate the impact of climate change on the Arctic ecosystem. Processes governing trace metal concentrations in rivers and streams remain relatively poorly understood, despite the importance of metals for aquatic ecosystems (Sherrell and Ross, 1999). This is particularly true for the huge arctic river systems like the Lena River as only few studies on the cycling of trace metals were carried out in the Siberian Arctic (Martin et al., 1993; Dai and Martin, 1995; Guieu et al., 1996; Garnier et al., 1996; Hölemann et al., 1999a). All studies have confirmed the pristine character of the Lena River which makes this river system an excellent region to study the natural metal cycling in arctic river systems without disturbance by anthropogenic pollution.

A weak point of all studies mentioned above is that they only cover the period from August to early October but not the high-discharge period at the end of May until the end of June (spring freshet). The high-discharge period is of particular importance because during June about 35% of the total annual discharge of the Lena River (AMAP, 1998) and more than 10 million tons of suspended matter (more than 60% of the annual input) flow into the Laptev Sea (Ivanov and Piskun, 1999). In contrast to the winter situation the spring freshet is characterized by an up to 500-fold increase in river discharge and a 10- to 20-fold increase in suspended matter concentration (SPM) (Cauwet and Sidorov, 1996). At the onset of the freshet the riverine discharge flows into the ice-covered SE Laptev Sea and forms a buoyant freshwater layer which spreads seaward beneath a 2 m thick sea ice cover (Pivovarov et al., 1999).

The dramatic change in the hydrologic regime is accompanied by distinct changes of river chemistry. The average mineralization decreases from 300–330 mg l^{-1} to 60–70 mg l^{-1}, the pH is reduced by approximately 0.5 units, and the concentration of dissolved organic carbon (DOC) can approach 1000 μM C or more (Cauwet and Sidorov, 1996; Pivovarov, pers. comm.). These changes in water chemistry can also control the partition of trace metals between suspended or bed load particles and dissolved phases (Stumm, 1992; Standring et al., 2002) and thus should have an affect on the concentration of dissolved and particulate trace metals in the river water. Also changes of the hydrologic flow path during the high-discharge period (Sherrell and Ross, 1999) and a release of dissolved metals from interstitial waters (Paucot and Wollast, 1997) are factors which may possibly alter the concentration of dissolved metals during the freshet.

Despite the fact that the spring freshet is apparently the most important period of the hydrological cycle of Siberian rivers, which dominates the fluxes of dissolved and particulate substances from land to the Arctic Ocean, it is also the least investigated period. So far, detailed studies of the high-flow period and the ice breakup processes in arctic rivers were carried out in the delta of the Colville River in Alaska (Hamilton et al., 1975; Walker, 1973), the Mackenzie estuary on the Beaufort shelf (Macdonald et al., 1995), the Liard River, a tributary of the Mackenzie River (Milburn and Prowse, 1996), and in the Lena Delta and the adjacent SE Laptev Sea (Pivovarov et al., 1999; Bareiss et al., 1999). But up to now no quantification of the trace metal discharge in the Lena River during the spring high-discharge period have been carried out. In this article we present the first dissolved and trace metal data measured in the Lena River and the adjacent SE Laptev Sea during the onset of the spring freshet. The data are compared with published data of metal concentrations measured in the Lena River delta during summer and with data from the low salinity surface waters (salinity$<$10) in the SE Laptev Sea which were taken during two summer expeditions to the Laptev Sea in 1993 and 1994 (Hölemann et al., 1995). The as yet unpublished complete trace metal data sets from these expeditions are available from the public data library PANGAEA (www.pangaea.de).

Detailed quantification of the trace metal discharge and its temporal/seasonal variability is justified by several important points: (1) annual flux estimates incorporating accurate data from all seasons are crucial for the formulation of watershed geochemical fluxes and are needed to establish a baseline against which to judge future changes of the geochemical cycles and pathways within the Arctic; (2) variability in riverine flux of metals to coastal marine ecosystems may play a key role in governing metal distributions and metal/biota interactions on continental shelves; and (3) temporal correlations of metal concentrations with fundamental variables may be used to infer potential mechanisms controlling trace metal fluxes (Sherrell and Ross, 1999).

2. Methods

2.1. Area description

The low-gradient continental shelf of the Laptev Sea covers 475,000 km^2 (0–200 m) (Treshnikov, 1985) and varies in width from 300 km in the western part to more than 500 km in the east (Fig. 1). The Lena–one of the major rivers that drain the Siberian Platform–is the major freshwater source for the Laptev Sea as runoff from the Lena accounts for more than 70% of the overall inflow of riverine waters into the Laptev Sea. In terms of water discharge, the Lena (525 km^3/year) ranks seventh in the world, and is together with the Ob second after the Yenisey among those rivers draining into the Arctic Ocean (Gordeev and Sidorov, 1993).

The Siberian rivers flow through large areas of permafrost and thus exhibit an arctic nival regime with very low flows during winter and a pronounced spring high flow generated by snowmelt. The mean monthly discharge in December is 2928 m^3/s (Global Runoff Data Centre, Koblenz, Germany; observational period 1935–1994 at Kyusyur). During the spring thaw in June the discharge increases to an average of 73,917 m^3/s (observed minimum 44,400 m^3/s, maximum 104,000 m^3/s). The monthly average discharge during June 1996 was 76,200 m^3/s (data from R-ArcticNet v3.0 published at www.r-arcticnet.sr.unh.edu) and, therefore, close to the long-term average for June.

Since the Lena flows north, the headwaters generally melt first during early May. Thus, the peak flow is transferred downstream and reaches the north several weeks later. After this high-flow period the discharge decreases again by approximately 50% (July 39,683 m^3/s and September 24,126 m^3/s).

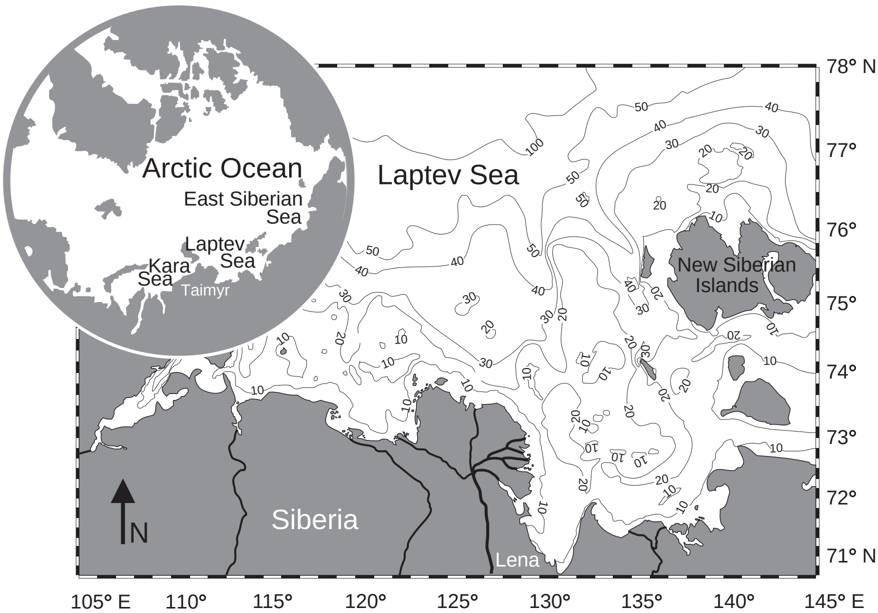

Fig. 1. Bathymetry of the Laptev Sea.

At the river mouth, the Lena branches off into several arms and forms an extensive delta covering an area of 32,000 km^2. The largest arms of the river are the Trofimov channel (62% of the total Lena river discharge), the Bykov (25%), the Olenek (7%), and the Tumat channels (6%). The floating ice in the river channels plays a significant role in the hydrology during the freshet because spring flash floods, which may cause strong river bed erosion, sediment redistribution and other major changes are usually caused by breaking dams of floating ice (AMAP, 1998).

On average the spring ice drift in the Lena river mouth begins on June 3 and takes 9 days (AMAP, 1998). When the spring freshet reaches the river mouth, the SE Laptev Sea is still ice covered by ~2 m thick coastal fast ice which is attached to the shore, and only near-shore areas start to open (Bareiss et al., 1999). During the freshet in spring 1996 the river water formed a steadily thickening, turbid freshwater layer under the fast ice of the SE Laptev Sea. This buoyant water mass was separated by a strong pycnocline from the underlying, less turbid brackish water (Pivovarov et al., 1999).

The water column of the SE Laptev Sea is also characterized by strong stratification during ice-free conditions (July until October). The river plume of the Lena river forms a 5–10 m thick surface layer with lower salinity (<20), which is separated by a strong halocline from the more saline bottom waters (Pivovarov et al., in press). In spite of large mesoscale variability in currents caused by changes in the wind field, a general slow counterclockwise (cyclonic) circulation is observed in the Laptev Sea in summer (Pivovarov et al., in press). In contrast to the high-discharge period when an immense load of SPM is transported within the river plume, most of the sediment transport during ice-free conditions takes place in the bottom nepheloid layer (Wegner et al., 2003). This bottom layer is suggested to develop during and briefly after the spring freshet of the Lena River.

2.2. Sampling

Sampling of water and total suspended matter (SPM) was undertaken within the framework of the German–Russian cooperation program "Laptev Sea System" in the Bykov channel in the delta of the Lena River and on the fast ice approximately 20 nautical miles east off the mouths of the Trofimov and Bykov distributaries during May and June 1996 (Fig. 2, stations 4 and 9). Two additional stations (8 and 11)

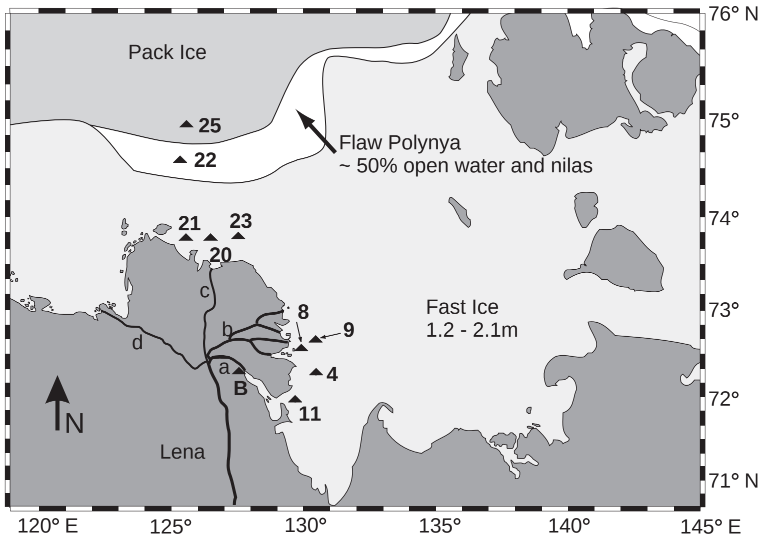

Fig. 2. Overview map of the ice conditions at the beginning of June 1996 (modified from Meteor-2(21) satellite images). Also shown are the hydrochemical sampling locations during the TRANSDRIFT IV expedition (triangles) and the largest distributaries of the Lena River (a = Bykov channel, b = Trofimov channel, c = Tumat channel, and d = Olenek channel).

were situated near the two major river outlets. Surveys at these stations were repeated 3 times to cover the winter situation and the beginning of the high-discharge period (dates are given in Table 1). The program was completed by measurements under the fast-ice north off the delta (stations 20, 21, and 23),

Table 1
Water depth, date and location of sampling, salinity, suspended matter (SPM), pH, particulate organic carbon (POC), concentration of dissolved metals (nM), and metal content in suspended matter ($\mu mol \cdot g^{-1}$ SPM) in samples taken during the TRANSDRIFT IV expedition in 1996 (< = concentration below detection limit).

Stat.	Depth, m	Date 1996	Position Lat. (N)/Long. (E)	Sal., PSU	pH	SPM, mg l^{-1}	POC %	Mn	Fe	Ni	Cu	Zn	Pb	Al	Mn	Fe	Ni	Cu	Zn	Pb
								nM						µmol/g						
								Dissolved						Particulate						
SE Laptev Sea																				
4A	3	6/06	72°14.2′/ 130°29.7′	0.9		1.6	15.2	231	813	18.6	11.5	16.2	0.14	2145	13.9	831	0.37	0.41	1.44	0.26
4A	10	6/06		21.9		1.4		144	298	15.3	13.8	22.8	0.10	254	6.4	104	0.68	0.28	1.59	0.13
4B	5	6/11		0.2		21.6	6.9	530	1728	11.8	32.9	29.7	0.39	2861	12.2	746	0.70	1.84	1.74	0.33
4B	10	6/11		3.7		11.0		1250	4001	10.2	16.8	17.6	0.39	2719	14.2	979	0.82	1.13	2.61	0.38
8A	3	6/03	72°30.9′/ 130°05.5′	0.2		10.2		420	1372	9.5	10.9	12.5	0.34	2851	18.0	920	0.33	0.53	3.95	0.38
8B	3	6/10		0.1		64.8		1498	9138	17.5	27.0	49.2	1.11	2869	6.2	367	0.37	0.25	1.33	0.13
9A	3	6/03	72°37.4′/ 130°29.5′	1.4		4.5	5.1	320	967	9.4	11.5	26.3	0.29	1755	7.9	578	0.41	0.33	1.80	0.22
9A	10	6/03		23.0		6.7		242	346	13.5	18.9	9.9	<	1903	10.3	639	0.65	0.46	1.65	1.22
9B	3	6/10		0.1		52.4		1465	6376	15.5	19.5	23.8	1.30	3074	5.6	404	0.41	0.24	0.87	0.17
9B	10	6/10		2.0		28.6		1855	6585	16.9	23.3	48.3	1.21	2868	10.1	733	0.70	0.55	1.80	0.24
11	3	5/22	71°53.0′/ 129°51.6′	5.9		0.3	25.3	109	734	17.4	13.5	14.2	0.10	1065	6.8	460	0.34	0.50	3.33	0.23
11A	3	6/06		0.2		10.5	3.2	750	2441	10.4	17.6	31.0	0.72	2686	16.7	856	0.77	0.50	2.68	0.38
11B	3	6/11		0.1		18.0	7.9	664	1766	17.2	26.0	53.5	0.58	2882	12.9	856	0.80	0.42	1.80	0.35
20	5	5/27	73°44.0′/ 126°30.7′	27.2		0.6	6.4	96	95	13.3	11.6	46.2	0.24	630	36.1	232	0.56	1.23	3.35	0.44
20A	3	6/12		1.8		13.9		1207	3861	10.2	16.7	12.7	0.48	2684	16.6	723	0.82	0.47	3.53	0.36
20A	7	6/12		27.7		10.4	6.2	375	471	11.1	12.9	9.6	<	2725	13.6	989	0.92	0.80	2.95	0.54
21	4	5/27	73°45.0′/ 125°29.6′	35.5		0.7	6.1	233	147	18.7	13.1	26.4	0.19	2572	16.4	969	0.89	0.58	2.34	0.23
22	10	5/27	74°32.7′/ 126°26.6′	24.8		0.5	19.6	29	29	9.5	8.0	14.7	0.10	796	42.0	228	0.78	0.55	2.80	0.12
23	5	5/29	73°45.0′/ 127°30.6′	24.3		0.6	16.5	98	127	14.8	12.9	18.0	0.14	657	24.7	197	0.32	1.21	0.90	0.23
25	10	5/29	74°51.5′/ 125°29.7′	31.9		0.6		15	43	8.5	7.9	15.7	0.10	861	12.2	237	0.32	0.53	0.89	0.13
Lena River—Bykov Channel/Lena-Nordenskjold station																				
B 3	5	5/21	72°12.0′/ 128°03.6′	0.3	7.5	1.1	2.4	84	643	18.2	11.5	14.2	0.10	1199	15.4	705	0.37	0.52	1.59	0.23
B 6	1	5/25		0.3		1.3	2.4	71	727	9.0	14.5	18.0	0.29	1134	24.5	818	0.48	0.70	2.22	0.36
B 8	1	5/28		0.3		0.9	2.6	171	1535	10.4	15.9	65.9	1.26	2105	14.5	786	2.37	0.86	5.95	2.57
B 9	1	5/29		0.2	7.3	1.7	3.3	82	629	8.7	12.4	23.4	0.19	2277	18.9	965	0.65	0.46	1.73	0.29
B 11	1	5/31		0.2		2.9	2.4	233	1207	8.5	13.8	14.1	0.29	2477	22.5	811	0.77	0.53	1.87	0.28
B 13	1	6/02		0.2	7.2	6.2	4.5	369	1304	10.4	12.4	25.4	0.19	2440	26.4	905	1.00	0.85	3.01	0.42
B 14	1	6/04		0.1		6.7	5.7	142	2187	10.9	39.0	22.9	0.48	2636	16.0	764	0.76	0.42	2.11	0.38
B 16	1	6/07		0.1	7.2	18.9	3.1	184	3322	12.9	23.3	5.7	1.06	2887	17.6	767	0.61	0.38	1.56	0.27
B 18	1	6/09		0.1		17.2	2.4	313	2574	13.1	22.2	9.0	0.53	2715	17.3	734	0.56	0.38	1.62	0.24
B 21	1	6/12		0.1	6.9	37.4	3.2	1471	5883	12.4	31.9	56.7	2.22	2880	11.6	686	0.66	0.41	1.74	0.24

within the ice-free coastal polynya north off the delta (station 22) and in the pack ice (station 25). All stations were reached with the means of helicopters.

Trace metal sampling was carried out from the ice through 9 cm drill holes with modified Teflon water samplers (Mercos) mounted on a metal-free wire. Water samples of 0.5 l were transported in the Teflon bottles to the laboratory where they were processed immediately. Samples from the river were taken near the "Lena-Nordenskjold" station (72°11′N, 128°03′E, station B in Fig. 2) on the right bank of the Bykov channel during the period from May 17 to June 13. When the river was completely ice-covered, sampling was carried out through drill holes from the ice at a distance of about 50 m from the bank. The depth of the river at this point was 10 m. During the initial phase of the spring thaw the existence of water on the river ice and strips of water between the bank and the ice made it impossible to take samples from the deep parts of the river channel. Water samples were then collected near the river bank at a water depth between 1 m and 2 m. To reduce the influence of local sources within the various channels, water and suspended matter samples were taken in the under-ice freshwater layer near the outlet of the Trofimov channel (station 8, 9) and the Bykov channel (station 11) where the fast ice was still thick enough to carry a helicopter. Detailed investigations of the nutrient chemistry and SPM concentration in the river water and the freshwater near the outlets indicate that no significant changes in river chemistry and SPM concentration took place between the sampling locations in the river channel and the under-ice freshwater layer (Pivovarov et al., 1999).

2.3. Analytical methods

To separate particulate and dissolved matter, vacuum filtration through pre-cleaned 0.4 μm polycarbonate filters (leached 3 times for 6 h in 3% subboiled HLC at 60 °C) was carried out within 8 h after sampling. Filtration was carried out directly from the water sampler by means of an in-line filtration system made of polycarbonate. To prevent air-borne contamination within the sampler the inflowing air was filtered and washed with acidified ultra clean water. After filtration of the water sample the filtrate was acidified to pH 2 and stored in acid-cleaned polyethylene bottles for further sample processing at the laboratory in Geesthacht (Germany). The filters were used to determine the particulate concentration of the trace elements.

All further analytical procedures including salt matrix elimination of the water samples and digestion of the suspended matter were carried out in clean rooms (class 1000) in the Research Center Geesthacht (GKSS, Germany). A detailed description of the sample pretreatment and the analytical quality control was published by Prange and Schirmacher (1999).

Mn, Fe, Ni, Cu, Zn, and Pb were measured by means of total-reflection X-ray fluorescence spectrometry (TXRF), a modified procedure of the conventional energy dispersive XRF (Prange and Schirmacher, 1999). Al was determined by means of coupled plasma mass spectrometry (ICP-MS). The accuracy and precision of the analytical methods for the determination of dissolved elements were tested using CASS-2, NASS-4, and SLRS-3 water standards (near-shore, open ocean seawater, and river water reference material, supplied by the National Research Council of Canada). Quality control for the analysis of particulate elements relied on sediment reference material from the National Research Council of Canada (MESS-1). For all elements the recovery rate was higher than 90%. Analytical precision was (i) better than 5% for Fe, (ii) 5–10% for Al, Mn, Ni, and Zn, (iii) 10–15% for Cu and Pb. In this study we present the results of the particle-bound elements Al, Mn, Fe, Ni, Cu, Zn, and Pb and the dissolved elements (i.e. operationally defined as metals which pass through a 0.4 μm filter) Mn, Fe, Ni, Cu, Zn and Pb.

The methods used for the determination of salinity (CTD probe), silicon concentration and suspended matter concentration (0.45 μm filtration) have been described in detail in Pivovarov et al. (1999). The pH of the water samples was measured with a portable pH-meter with a resolution of 0.01 pH units.

3. Results and discussion

3.1. Hydrography and water chemistry before the high discharge period (winter situation)

All data about the location of the sampling sites, hydrography and the dissolved and particulate trace metal concentrations are given in Table 1.

The oceanographic surveys along the N–S transect east off the Lena Delta revealed a distinct two-layer stratification of the water column. During the first surveys on May 21 and 22, 1996, the salinity and temperature distribution at station 9–situated 50 km west of the main river outlet–showed an approx. 2 m thick layer of water with salinities between 6 and 10 below the ~2 m thick fast-ice cover (Fig. 3). Between 4 m and 10 m the salinity increased to values above 27. The SPM concentration in the upper 10 m of the water column was less than 2 $mg \cdot l^{-1}$. Only in the bottom mixed layer between 10 m and the seafloor at 16 m were SPM concentrations higher than 13 $mg \cdot l^{-1}$. The whole water column was characterized by low temperatures close to the freezing point.

Suspended matter concentrations below 2 $mg \cdot l^{-1}$ were also recorded in the Lena river water in the Bykov branch (Table 1). The river water and the low-salinity water near the river mouth showed high silicon concentrations above 140 μM Si (Fig. 4), which is 2 times higher than the mean concentration during summer (Lara et al., 1998). With the exception of Ni the dissolved concentrations of all trace metals investigated in river water and in the low-salinity surface water near the river outlets (station 9 and 11) were in the same range as published summer concentrations (Fig. 4). Lowest dissolved concentrations of trace metals were found on the mid-shelf in the polynya region and under the pack ice 80 nautical miles north of the delta (stations 22 and 25).

A peculiar hydrographic feature was observed in the shallow coastal region north of the Lena Delta. At station 21 high-salinity bottom water (>35) was observed near the seabed at 4 m water depth. During summer the coastal region near the delta is usually occupied by low-salinity waters (<10). A possible cause for the occurrence of high-salinity bottom waters near one of the major outlets of the Lena river region is the supply of salt-enriched brines that result from ice formation (Smith et al., 1990). In the low-energy environment under the coastal fast-ice the dense brines can accumulate in morphological depressions on the shallow inner shelf. Despite the brine-induced high salinity the concentrations of trace metals showed no higher levels if compared to the coastal waters at the stations 8, 11 and 20 near the delta.

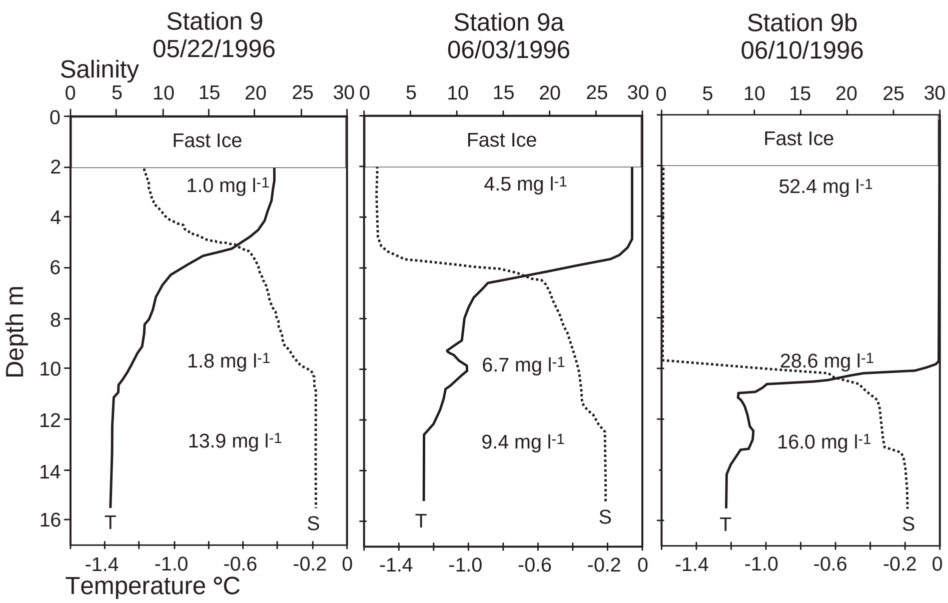

Fig. 3. Time series of the salinity/temperature profiles and suspended matter concentrations from station 9 (a,b) situated approx. 15 nautical miles west of the Trofimov channel under a 2 m thick fast ice cover. The repeated sampling covered the situation before the high flow (May 22), at the initial phase of the spring freshet (June 3), and during the freshet (June 10).

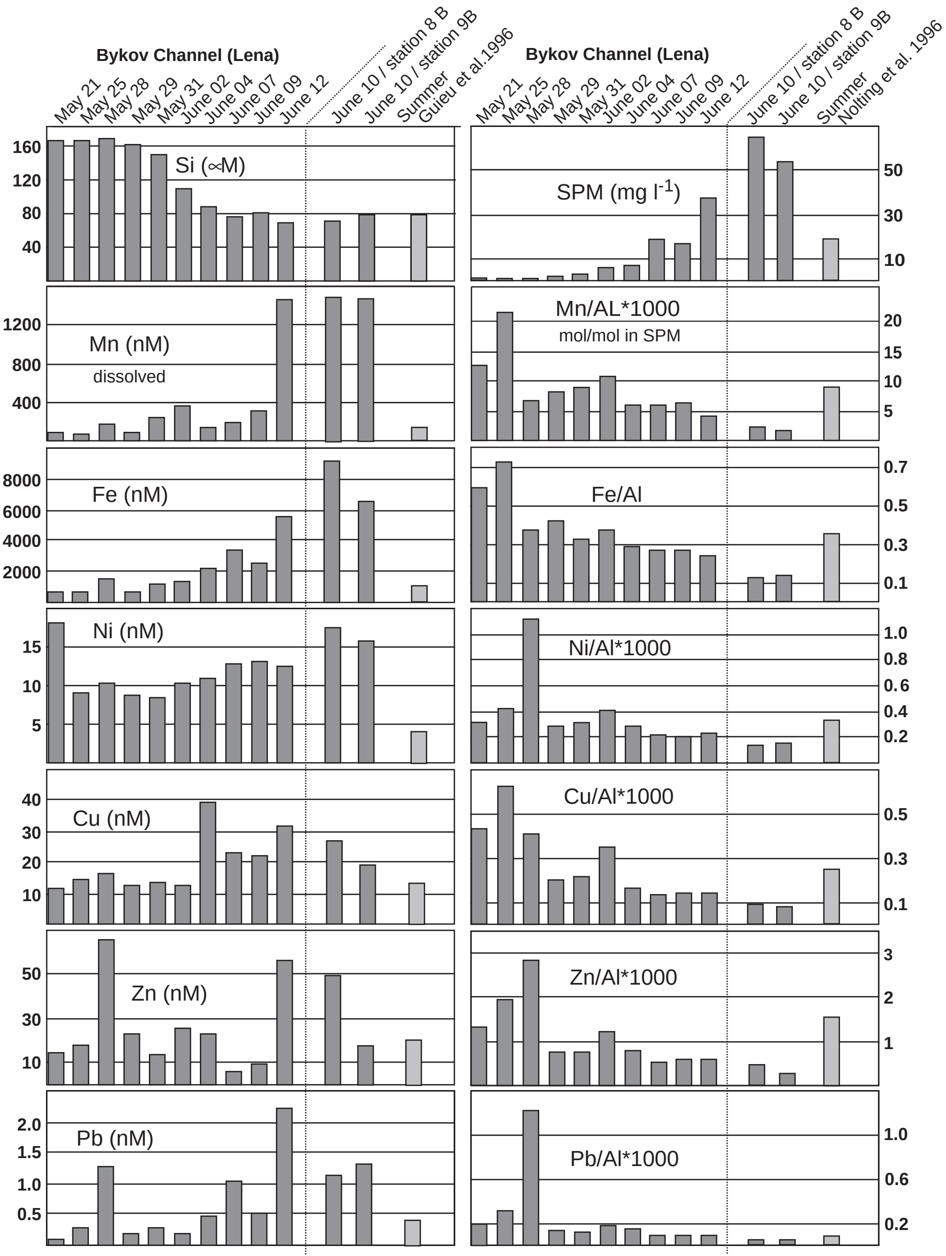

Fig. 4. Concentration of dissolved Mn, Fe, Ni, Cu, Zn, Pb, Si, suspended matter, and metal aluminium ratios (mol/mol) of suspended matter in the Bykov channel before and during the spring high flow, and near the mouth of the Trofimov channel during the freshet. Data for the summer concentration of dissolved Si were taken from Lara et al. (1998).

Comparing the high silicon concentration with published winter data from the Lena River (Cauwet and Sidorov, 1996) we conclude that the hydrographic situation on May 21 and 22 reflects the typical winter situation in the river Lena and the coastal Laptev Sea. During winter the river water is derived mostly from the flow of groundwater (Gordeev and Sidorov, 1993). The pH of the 'winter' river water was ~7.5

and the oxygen saturation was below 60% (Pivovarov et al., 1999). Like the concentration of dissolved trace metals, trace element concentrations in SPM (Table 2) also fall into the range of typical concentrations of suspended matter measured during the summer months (Nolting et al., 1996; Rachold, 1999) and of surficial sediments near the river mouth (Hölemann et al., 1999b). To obtain a more detailed understanding of the composition of suspended matter and its variability during the spring high flow, particulate trace metals were normalized to aluminium (Fig. 4). This method allows for the elimination, to a large extend, of the effect of the grain size on the distribution of particulate elements, which accumulate preferentially on fine particles (Paucot and Wollast, 1997). Before the freshet, however, the particulate Al concentration in the low-turbidity river water was approximately 2 times less than the average Al concentration during the freshet (Table 1) and in summer (Rachold, 1999). This resulted in increased trace metal/Al ratios before the onset of the high discharge period (Fig. 4). The low Al concentrations were not accompanied by a higher proportion of particulate organic matter because the concentration of particulate organic carbon (POC) showed only little variability in the course of the spring high flow. The data show that the Fe and Mn/Al ratios during low discharge are approximately 2 times higher than the average crustal ratio (Krauskopf, 1979, pp. 544–545). This suggests that during the low-discharge winter period (SPM <2 mg $\cdot$ l^{-1}) differences in the SPM particle spectrum with a higher proportion of small size Fe/Mn oxyhydroxide particles and coatings (Lion et al., 1982) are probably the main factor controlling the chemical variability of river SPM.

3.2. Initial phase of the spring high flow in the Bykov branch

The onset of the spring high flow in the Bykov branch was first noted on May 26 when freshwater flowed onto the ice-covered river through small cracks in the ice. Within 4 h the water on top of the ice was approximately 1.5 m deep. By the following day buoyancy effects had lifted the ice to the surface, draining the river water from the ice surface. The water level within the channel rose by 1.5 m but large areas of the ice cover of the Bykov branch were still in place, with an isolated open water channel in the middle of the branch.

The first water sampling for the determination of trace metal concentrations was conducted on May 28

Table 2
Comparison of dissolved and particulate trace metal concentrations during the freshet (this study) and data from the river Lena and SE Laptev Sea obtained during the summer season from July to October

Dissolved trace elements in the Lena River and SE Laptev Sea	Mn, nM	Fe, nM	Ni, nM	Cu, nM	Zn, nM	Pb, nM
Lena spring freshet 1996 stations 8B, 9B, B21	1478 ± 18	7132 ± 1754	15.2 ± 2.6	26.2 ± 6.3	43.3 ± 17.3	1.55 ± 0.59
Lena River—October 1995 (Hölemann et al., 1999a)	99	1494	5.9	11.9	15.4	0.51
Lena River—at Kyusyur September 1991 (Guieu et al., 1996)		866	4.3	13.5	14.3	0.4
Lena River—September 1989 (Martin et al., 1993)		410	5.2	9.7	5.3	0.08
Lena river plume (salinity < 10) Sept. 1993 (Hölemann et al., 1995)	111 ± 70	621 ± 275	8.1 ± 2.3	10.4 ± 5.6	8.2 ± 5.6	0.28 ± 0.02
Lena Delta and coastal zone September 1991 (Guieu et al., 1996)		642 ± 208	4.4 ± 0.1	13.8 ± 1.6	1.2 ± 1.0	0.2–0.3

Particulate trace elements in the Lena River and SE Laptev Sea	Mn, μmol/g SPM	Fe, μmol/g SPM	Ni, μmol/g SPM	Cu, μmol/g SPM	Zn, μmol/g SPM	Pb, μmol/g SPM
Lena spring freshet 1996 stations 8B, 9B, B21	7.8 ± 3.3	486 ± 174	0.48 ± 0.16	0.30 ± 0.01	1.31 ± 0.44	0.18 ± 0.06
Lena River 1994–1996 (Rachold, 1999)	29.5	340	0.90	0.55	2.16	0.12
Lena River—September 1991 (Nolting et al., 1996)	15.3–22.5	591–877	0.41–0.63	0.41–0.61	2.75–3.32	0.15–0.18

within a strip of open water between the river bank and the ice. If compared to the measurements before the flooding, the river water sampled on May 28 showed significantly higher concentrations of dissolved Zn and Pb, and particulate Al, Ni, Zn and Pb (Table 1). We suggest that the admixture of melt water from the snow cover of the river which melted during the flooding of the river ice is the cause for this short-term increase in Ni, Zn, and Pb. This is also supported by low silicon concentrations in the river water on May 26 (Pivovarov et al., 1999). The snow cover accumulates trace metals by wet and dry deposition of natural and anthropogenic aerosols for a period of more than 8 months (AMAP, 1998). Therefore, the rapid melting of the snow cover on the river ice could result in a temporary input of trace metals to the river water.

On May 29, the silicon and trace metal concentration as well as the pH again reached the values that had been measured before the water level of the Bykov channel rose. The SPM concentration was 2 times higher, and the Al concentration increased by approximately 100% if compared to the concentrations before the flooding of the river ice. The higher particulate Al concentrations led to increased element/aluminium ratios that are typical for chemical composition of riverine suspended matter during summer (Rachold, 1999). This points to a change in the SPM particle assemblage during the initial phase of the spring high flow which might be the result of the increased stream velocity and a subsequent erosion of river bed sediments.

Even though the water level in the channel rose by 1.5 m, the river water chemistry showed the most pronounced changes only several days later (Fig. 4). This suggests that during the initial phase of the spring high flow the winter water was flushed out from the river branches by the approaching flood wave of the spring snowmelt. Thus changes in river water chemistry were most pronounced only after the freshet reached the sampling sites.

3.3. Hydrological and chemical regime during the freshet

On June 12 the flow within the Bykov channel increased significantly, large areas of the ice in the channel broke up and moved downstream. The SPM concentration increased from 2 $mg \cdot l^{-1}$ to 37 $mg \cdot l^{-1}$ on June 12, which is twice the typical summer concentration. The silicon concentration reached the typical summer values of below 80 μM Si. These changes were accompanied by a decrease of river water pH by 0.5 units to a pH of 6.9. This decrease in river water pH is a characteristic phenomenon of the spring freshet in the Lena River (Pivovarov, pers. comm.).

Already on June 10 high SPM concentrations (>50 $mg \cdot l^{-1}$) were recorded in the freshwater layer under the ice in front of the mouth of the Trofimov channel (stations 8b and 9b) while the SPM concentration in the Bykov channel was still below 20 $mg \cdot l^{-1}$. According to Gordeev and Sidorov (1993), suspended matter concentrations between 60 and 70 $mg \cdot l^{-1}$ are typical for the high-discharge period. Based on these observations we assume that the flood wave of the spring freshet reached the mouth of the Trofimov branch approximately 3 days earlier than our sampling location in the Bykov channel. This is also supported by the observation that during the freshet the discharge of the Trofimov branch is approximately 2 times higher than the discharge of the Bykov branch (Ivanov and Piskun, 1999).

Compared to the concentration measured during the low flow all dissolved metals showed a significant increase in concentration (Fig. 4) when the freshet reached the sampling sites. Mn, Fe, and Pb concentrations were about 10 to 20 times higher during the high flow, while the concentrations of Zn, Cu, and Ni were only increased by a factor of about two to four. The highest dissolved trace metal concentrations were not found in the Bykov channel but in the freshwater layer in front of the mouth of the Trofimov channel (stations 8b and 9b). In the low salinity water mass the dissolved concentrations of Fe, Mn, Pb and Zn are significantly correlated with the SPM content ($p<0.01$ for Fe, Mn, Pb; $p<0.05$ for Zn). Ni showed no significant correlation with SPM. This is caused by increased concentrations of Ni in waters with low and moderate SPM content (11B, 4A, and in the Bykov channel on May 21). Although the concentration of Zn and Pb are also increased in the sample from station 11B, we suppose that the higher Ni concentrations were not caused by contamination during sampling, but come from local sources that could not be identified. If the three stations are excluded from the data set the correlation between Ni and SPM is also significant on a 0.01 level. If station 9B is removed from the data set because it shows low dissolved trace element concentration at high SPM, Cu is also correlated to SPM at the 0.05 level.

In the same low-salinity water mass the element/Al ratios of particulate Fe, Mn, Pb, Ni, and Zn are negatively correlated with SPM (for Fe/Al, Mn/Al, Pb/Al significance at the 0.01 level; Zn/Al and Ni/Al at the 0.05 level). This supports the conclusion that the mobilization of metals from suspended particulate matter is the driving force for the observed high concentrations of dissolved Fe, Mn, Zn and Pb in the water of the Lena River during the spring freshet. A possible explanation for the mobilization could be the dissolution of Fe/Mn oxyhydroxide coatings on mineral surfaces because of a decreasing pH (Lion et al., 1982; Stumm, 1992). Because Fe/Mn oxyhydroxide surfaces act as scavengers for other trace metals, a pH-driven desorption of these metals from the coatings can result in increased dissolved trace metal concentrations (Lion et al., 1982). This is also supported by a strong positive correlation (<0.001) between all trace metal/Al ratios and Fe/Al and a negative correlation between the dissolved concentration of Mn, Fe, Cu and Pb with the Fe/Al ratio.

Although our data indicate that benthic input of dissolved trace metals due to the erosive action of ice as proposed by Scrimgeour et al. (1994) for nutrients seems not to be the cause for the high concentrations of trace metals during the spring high flow, this mechanism can also contribute to the input of trace metals especially during the first phase of the freshet when the river ice breaks up.

Garnier et al. (1996) demonstrated that in the Lena River trace metal partitioning between the dissolved and the particulate phase is not controlled by dissolved organic matter (DOM). While DOM is unlikely to control trace metal partitioning during the freshet, organic matter of colloidal size may play an important role for the chemical behavior of dissolved trace metals because a significant amount of the ‘dissolved’ (<0.45 μm) trace metals in Siberian rivers is actually associated with colloidal material (Dai and Martin, 1995).

3.4. The importance of the freshet for the flux of trace metals to the SE Laptev Sea

If compared to the concentrations of dissolved trace metals in the Lena River measured during September 1991 (station 1 in Guieu et al., 1996), the dissolved concentrations of trace metals during the freshet are significantly higher (Table 2). The results presented by Guieu et al. (1996) are in agreement with trace metal data that were obtained during two expeditions to the Lena river plume in the SE Laptev Sea during August/September 1993 and 1994. Like the concentration in the river water, the concentrations in the river plume measured during the time from August to September also showed significantly lower values than those recorded in the river plume during the freshet.

A budget of riverine fluxes of particulate and dissolved trace elements to the Arctic Ocean was published by Gordeev (2000). The trace metal concentrations used for the evaluation of fluxes from the Lena River were based on data from summer and fall published by Martin et al. (1993) and Guieu et al. (1996). Also the studies on the geochemical behavior of different trace elements in the river/sea mixing zone cited in Gordeev (2000) were solely from the period after the high discharge in June. Our data show that the metal budgets for the river Lena that did not include data from the spring high-flow period underestimate the fluxes of dissolved trace metals from the Siberian rivers to the Arctic Ocean. As an example according to Gordeev (2000) the average yearly discharge of dissolved Fe by the river Lena is a 19×10^3 t year^{-1}. If we assume that the dissolved Fe concentration during the freshet (June, discharge 77,900 m^3 s^{-1}) is ~6000 nM, the discharge of Fe during June alone would be as high as 67×10^3 t. Very low dissolved Zn concentrations of 1.2 nM from the Lena river plume (published by Guieu et al., 1996) were taken by Gordeev (2000) to estimate an annual Zn discharge of 40 t. Our data show that during the high discharge period the dissolved Zn concentration can exceed 50 nM. If this concentration is characteristic for the freshet the calculated dissolved Zn input in June will be more than 600 t. The discrepancies that are caused by the strong seasonal nature of riverine discharge accentuate the need for data from all discharge periods before realistic budgets of geochemical fluxes can be established.

Our observations show that the pronounced density stratification of the water column in the SE Laptev Sea caused the transport of dissolved trace metals in an under-ice freshwater plume. The transport of dissolved trace metals in the freshwater layer under the ice has direct consequences for the cycling of metals on the broad shelf of the Laptev Sea. During the high-discharge period in June only the fast ice cover in the direct vicinity of the Lena disintegrates (Bareiss et al., 1999). Sea-ice retreat in the Laptev Sea commences on average on July 4, with the summer minimum being reached 66 days later (Bareiss et al., 1999). The ice cover prevents the wind-forced mixing of the freshwater layer with the brackish-marine water masses below the pycnocline. Only in the area of the coastal polynya or after the decay of the sea ice could atmospheric forcing lead to the breakdown of the strong density stratification. Assuming that at the end of the freshet the freshwater plume with its high levels of dissolved trace metals occupies large areas of the SE Laptev Sea, the plume must be supposed to have an effect on the marine ecosystem as the high-discharge period coincides with the onset of the phytoplankton spring bloom (Tuschling, 2000).

Guieu et al. (1996) documented that for Zn and Pb a simple mixing of the Lena river waters with the arctic waters is observed. This means that even when the river plume with its high levels of dissolved Zn (50 nM) mixes with arctic waters (~3 nM (Guieu et al., 1996)), the low salinity surface (salinity < 15) waters that are characteristic for the inner shelf region of the eastern Laptev Sea should have a dissolved Zn concentration of more than 20 nM at the end of June. While these levels are not expected to be toxic, they would be important for the overall trace nutrient status of phytoplankton during the spring bloom (Sunda and Huntsman, 1998).

Our knowledge of the transport and cycling of trace metals in the Arctic Ocean is still sketchy. Future research should focus on hydrographic information and biogeochemical data from important seasonal phases such as the spring freshet of arctic rivers and the beginning of the phytoplankton spring bloom in the coastal Arctic Ocean. Because trace metal data from these periods are sparse, more observations are urgently needed.

4. Conclusions

(1) The results show that concentrations of dissolved Fe, Mn, Cu, Ni, Zn, and Pb in the river Lena during the spring freshet in 1996 were significantly higher than published summer concentrations. In the particulate phase the Al-normalized concentrations of Fe, Mn, Pb, Ni, and Zn are negatively correlated with SPM. Because the increase of dissolved trace metals is accompanied by a decrease in the particulate phase, we suggest that the variability in the trace metal dissolved/particulate partitioning is essentially controlled by the mobilization of metals from suspended particles.

(2) During June alone about 35% of the total annual flow of the river Lena flows into the Laptev Sea. Previously published metal budgets for the river Lena that did not incorporate data from the spring high flow period, therefore, underestimate the fluxes of dissolved trace metals from the Siberian rivers to the Arctic Ocean. As an example the estimated input of dissolved Fe in June 1996 is approximately 4.5 times higher than the average annual dissolved Fe input calculated by Gordeev (2000).

(3) Dissolved metals are transported within the Laptev Sea in an under-ice river plume. The ice cover prevents the wind-forced mixing of the freshwater layer, only in the area of the coastal polynya and after the decay of the sea ice can atmospheric forcing break down the strong density stratification. Hence, in the SE Laptev Sea in spring, mixing-zone processes which can cause changes in the metal distribution between the dissolved and particulate phase occur in mid-shelf areas far away from the river mouth.

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